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Face-specific Inhibition of Crystal Growth with Bidentate Ligands: A Lack of Kinetic Competition Between Succinate and Tartrate

Dan Druffel

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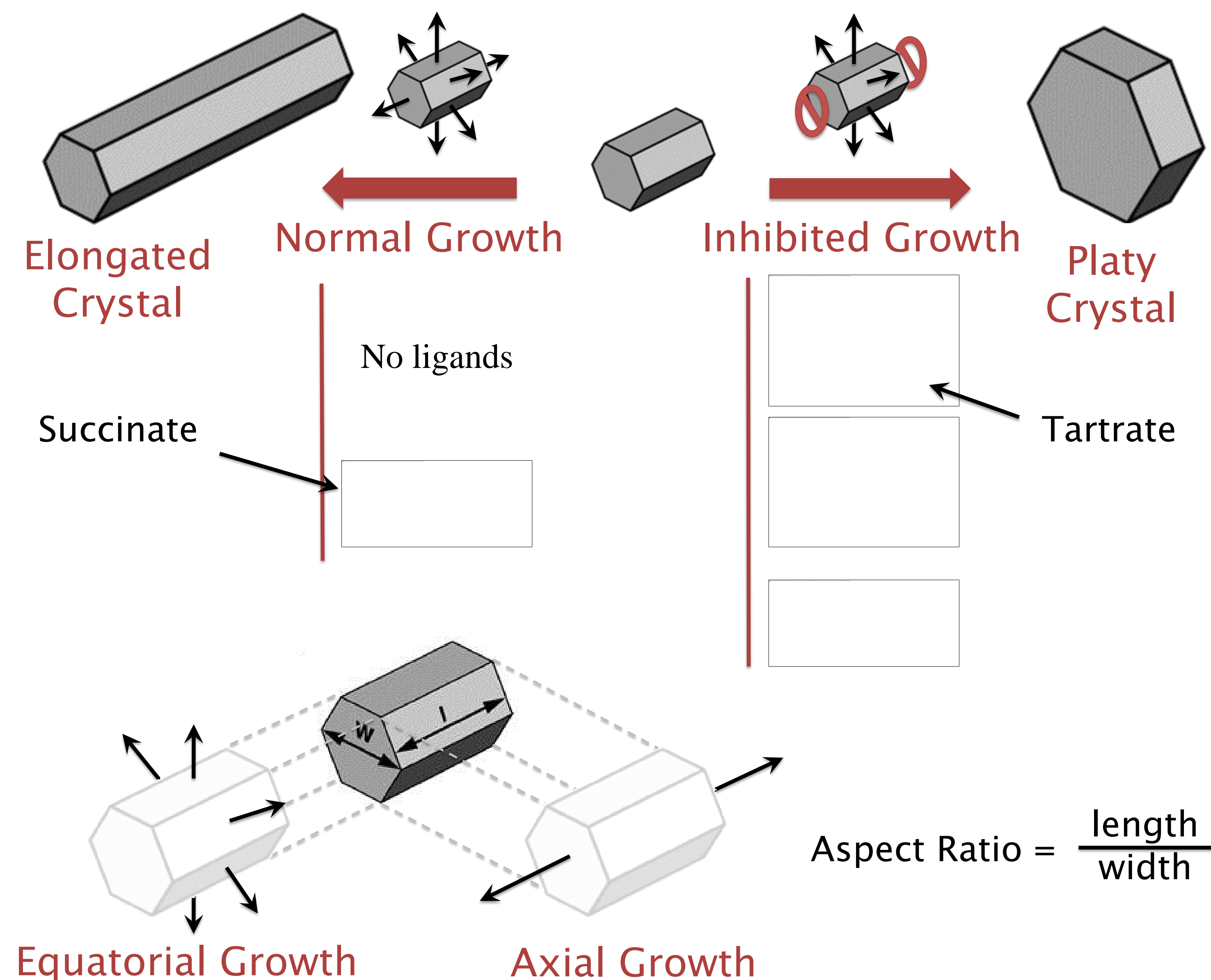
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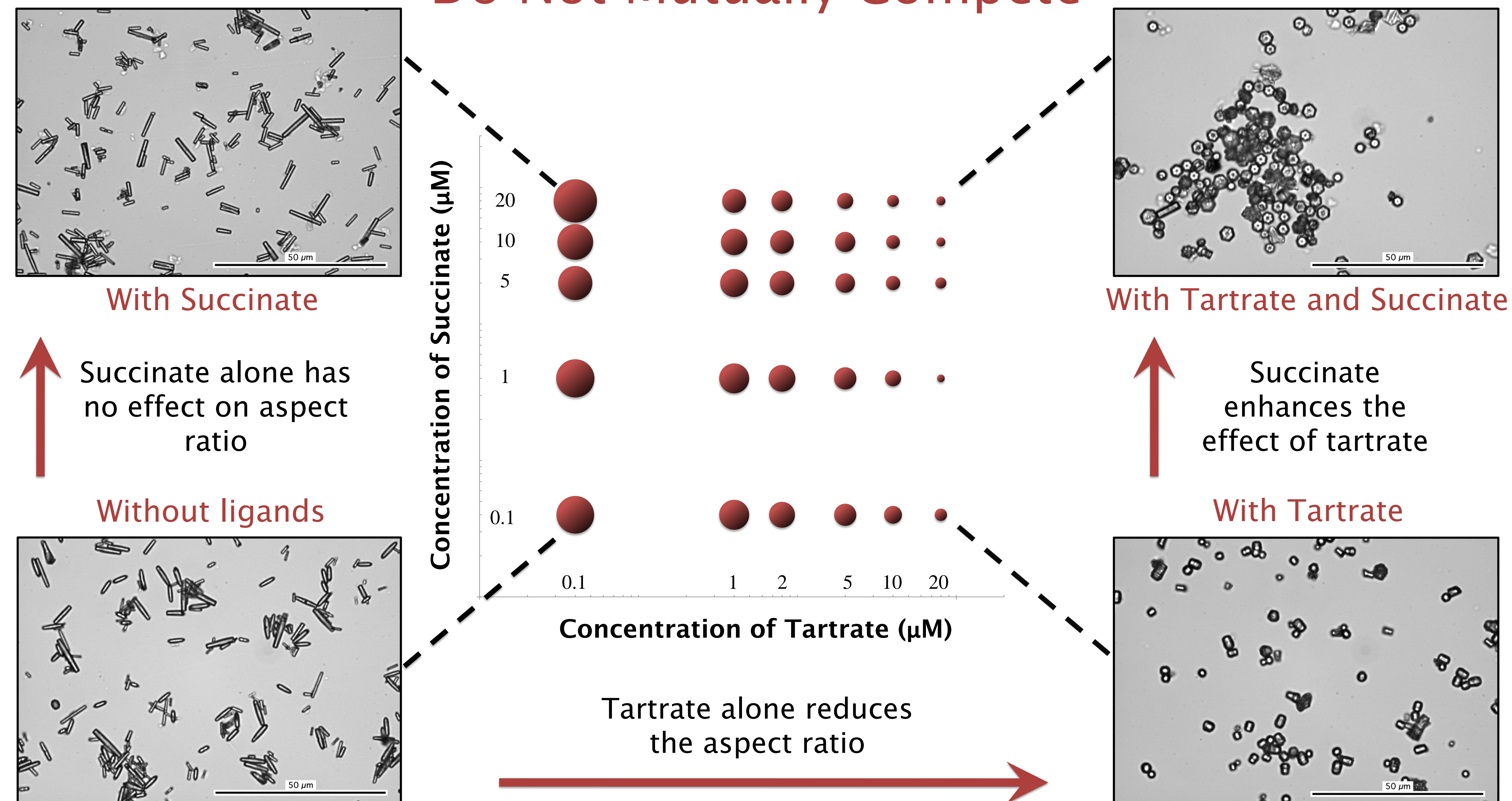
Face-specific Inhibition of Crystal Growth with Bidentate Ligands: A Lack of Kinetic Competition Between Succinate and Tartrate

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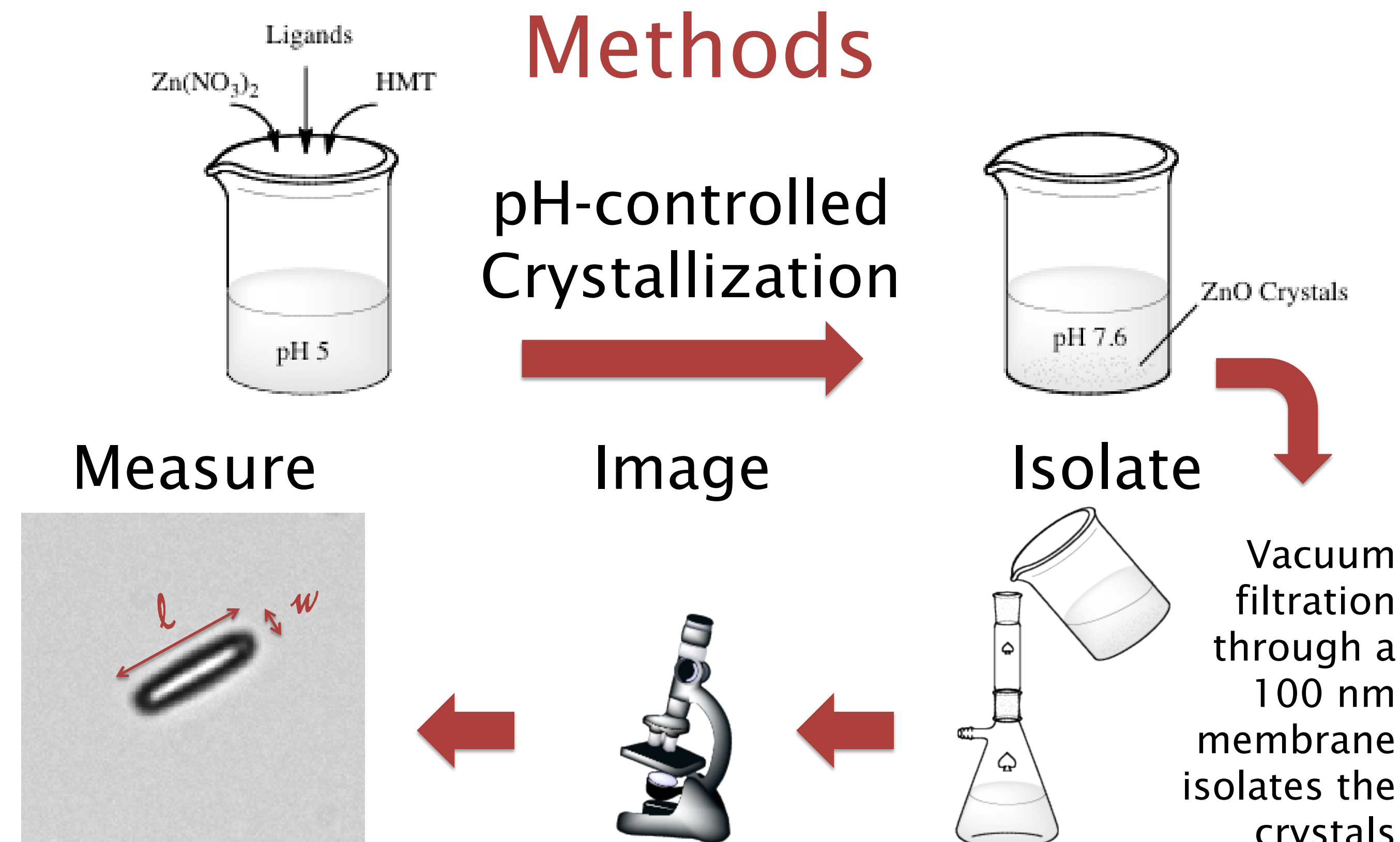
Face-specific Inhibition Enables Shape Control



Succinate and Tartrate Do Not Mutually Compete



Methods



Aspect ratio is a measure of face-specific inhibition

Why doesn't succinate inhibit axial growth?

Hypothesis:

Succinate has lower affinity for hexagonal face than other ligands

- ✓ consistent with structure
- ✓ consistent with succinate alone
- ✓ consistent with tartrate alone
- ✗ consistent with both ligands

Hypothesis:

Succinate has an equal affinity but does not prevent incorporation

- ✗ consistent with structure
- ✓ consistent with succinate alone
- ✓ consistent with tartrate alone
- ✓ consistent with both ligands

Abstract

The mechanism of face-specific, crystal-growth inhibition by bidentate ligands was investigated by studying kinetic competition between two bidentate ligands — succinate and tartrate — for zinc oxide crystal surfaces. ZnO microcrystals were grown from aqueous zinc nitrate solutions at 90 °C after a controlled pH shift to neutral-pH conditions and were isolated by vacuum filtration. Crystals were imaged by optical microscopy and their dimensions were quantified. In the absence of ligand, crystals were shaped like long, hexagonal prisms. Addition of sodium tartrate (20 μM) to the growth solution resulted in flat, plate-like crystals, suggesting that tartrate inhibits axial growth selectively by binding to the crystals' hexagonal faces. In contrast, the addition of sodium succinate alone yielded long hexagonal microcrystals, suggesting that succinate lacks affinity for the crystal surface. When both tartrate and succinate were added, competition was not observed, they instead demonstrated a surprising synergistic interaction: when tartrate concentration was high (10–20 μM), adding succinate (1–20 μM) enhanced the shape-control activity of tartrate further. This result suggests that simple competitive inhibition is not an appropriate model for the surface chemistry that underlies shape control.

Acknowledgements

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